Dipalladium Bis(μ-isopropylthiolato) Complexes with a $[Pd_2S_2]$ Core Supported by N-Heterocyclic Carbenes

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The reaction of $Pd(OAc)_2$ with 1,3-dibenzylbenzimidazolium bromide (**A**) and 1-propyl-3-methylbenzimidazolium iodide (**B**) afforded the dihalo-bis(carbene) complexes *cis*-$[PdBr_2(Bz_2\text{-bimy})_2]$ (**1**) and *cis*-$[PdI_2(Pr,Me\text{-bimy})_2]$ (**2**), respectively. Halide substitution of **1** and **2** with AgO_2CCH_3 gave the mixed diacetato-bis(carbene) complexes *cis*-$[Pd(O_2CCH_3)_2(Bz_2\text{-bimy})_2]$ (**3**) and *cis*-$[Pd(O_2CCH_3)_2(Pr,Me\text{-bimy})_2]$ (**4**). In situ deprotonation of isopropylthiol with the mixed carbene-carboxylato complexes **3** and **4** yielded the novel dipalladium complexes $[Pd_2(\mu\text{-iPr-S})_2(Bz_2\text{-bimy})_4](BF_4)_2$ (**5**) and $[Pd_2(\mu\text{-iPr-S})_2(Pr,Me\text{-bimy})_4](BF_4)_2$ (**6**) with a $[Pd_2S_2]$ core solely supported by N-heterocyclic carbenes. All compounds have been fully characterized by multinuclei NMR spectroscopies and ESI mass spectrometry. The solid state molecular structures of complexes **2**, **3**, **5**, and **6** have also been confirmed by X-ray diffraction studies.

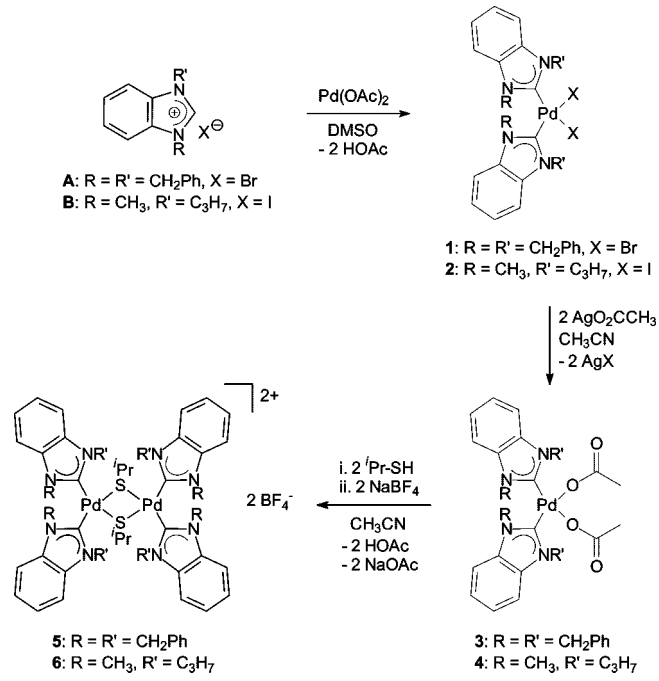
Introduction

Transition metal complexes of N-heterocyclic carbenes (NHCs) have been investigated in recent years with great intensity due to their unique properties especially in the field of organometallic catalysis.[1] In particular, mono- and bis(carbene) complexes of transition metals with chloro, bromo, and iodo ligands have been studied in more detail, while other anionic co-ligands remain relatively rare in NHC chemistry. Recently, we reported the straightforward synthesis of mixed carboxylato-carbene complexes of palladium(II) and their application as catalyst precursors for the Mizoroki−Heck reaction.[2] In addition, these complexes also show an interesting trans–cis isomerism. As an extension of our research, we herein report on the reactivity study of such mixed diacetato-bis(carbene) complexes toward aliphatic thiols, which offers an easy access to novel dinuclear Pd(II) complexes bearing a $[Pd_2S_2]$ core solely supported by NHCs.

Results and Discussion

Palladium(II)-NHC Precursor Complexes. The synthetic pathway for all complexes described in this work is outlined in Scheme 1. The in situ deprotonation of benzimidazolium salts with $Pd(OAc)_2$ as basic metal precursor has become a general method for the preparation of Pd(II)-benzimidazolin-2-ylidene complexes. Correspondingly, we obtained the dihalo-bis(carbene) complexes *cis*-$[PdBr_2(Bz_2\text{-bimy})_2]$ (**1**) and *cis*-$[PdI_2(Pr,Me\text{-bimy})_2]$ (**2**) using the salts 1,3-dibenzylbenzimidazolium bromide (**A**) and 1-propyl-3-methylbenzimidazolium iodide[3] (**B**) in DMSO at elevated temperatures. These two carbene precursors have been chosen due to the ease of their preparation and also to demonstrate the versatility of this methodology for both symmetrically and unsymmetrically substituted salts with bromide or iodide anions. The formation of complexes **1** and **2**, which have been isolated as white or off-white solids, was confirmed by ^1H NMR spectroscopy. The absence of a downfield signal characteristic for the NCHN protons in the salts **A** and **B** indicates a successful formation of Pd(II) carbene complexes. The benzylic protons in **1** are diastereotopic and resonate as two doublets centered at 6.38 and 5.66 ppm,

Scheme 1. Synthetic Pathway for Dipalladium Complexes



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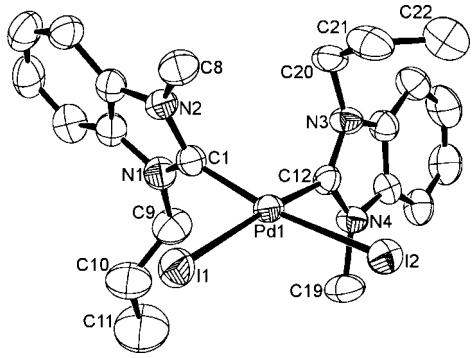

Figure 1. Molecular structure of complex **2**·0.5Et_2O showing 50% probability ellipsoids. Hydrogen atoms and the solvent molecule have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 1.992(6), Pd1−C12 1.995(5), Pd1−I1 2.6431(6), Pd1−I2 2.6664(6), C1−N1 1.352(7), C1−N2 1.359(7), C12−N3 1.354(7), C12−N4 1.349(7); C1−Pd1−C12 92.4(2), I1−Pd1−I2 93.893(18), C12−Pd1−I2 87.99(15), C1−Pd1−I1 87.27(15), C1−Pd1−I2 169.64(17), C12−Pd1−I1 171.54(17).

respectively, with a coupling constant of ^2J(H,H) = 15.78 Hz. This diastereotopy determined by molecular symmetry points to a cis arrangement of the two carbene ligands. ^{13}C NMR data of **1**, on the other hand, could not be obtained due to its extremely low solubility in common organic solvents. The ^{1}H NMR spectrum of **2** is more complicated due to the unsymmetrical nature of the carbene ligand. Similar to complex **1**, the methylene protons of complex **2** are also diastereotopic, giving rise to two broad multiplets for each CH_2 group, again indicating a cis arrangement. In addition, two sets for each signal are observed with an intensity ratio of 1:0.54, indicating the existence of cis-anti and cis-syn isomers in solution, which is in line with a restricted rotation of the NHC ligands due to steric bulk. The major resonances have been tentatively assigned to the sterically more favorable cis-anti isomer. The ^{13}C NMR spectrum of **2** also shows two sets of signals corroborating the existence of an isomeric pair. The two carbenoid carbon atoms have similar chemical shifts of 173.9 and 174.3 ppm, which are in the range typically found for cis-configured Pd(II) dihalo-bis(carbene) complexes of benzimidazolin-2-ylidene ligands.[4] The formation of **1** and **2** has also been confirmed by positive mode ESI mass spectrometry, which shows an isotopic envelope at m/z = 783 and 581, respectively, for the $[M - X]^+$ cations resulting from loss of one halo ligand.

Single crystals of solvate **2**·0.5Et_2O suitable for X-ray diffraction were obtained from diffusion of diethyl ether into a saturated DMF solution at ambient temperature, and its molecular structure is shown in Figure 1. The mononuclear complex contains a Pd(II) center that is coordinated by two NHC and two iodo ligands in a distorted square-planar fashion. The distortion from perfect square-planar geometry is quantified by a dihedral angle of 13° between the Pd−C1−C12 and the Pd−I1−I2 planes. The two unsymmetrically substituted carbene ligands are found in a cis-anti arrangement to each other and are oriented almost perpendicularly to the mean PdC_2I_2 coordination plane with dihedral angles of 71° and 74°, respectively. The Pd−$C_{carbene}$ (1.992(6) and 1.995(5) Å) and the Pd−I (2.6431(6) and 2.6664(6) Å) bond lengths are in the same range as observed for other *cis*-benzimidazolin-2-ylidene Pd(II) complexes.[4]

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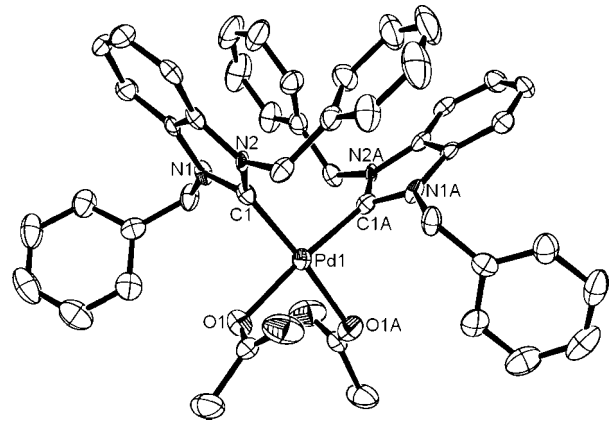

Figure 2. Molecular structure of complex **3** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 1.985(6), Pd1−O1 2.048(5), C1−N1 1.338(8), C1−N2 1.361(8); C1−Pd1−C1A 93.4(4), C1−Pd1−O1 90.6(2), O1−Pd1−O1A 85.7(3), C1−Pd1−O1A 174.2(2).

Halide substitution of **1** and **2** with AgO_2CCH_3 afforded the mixed diacetato-bis(carbene) complexes *cis*-[$Pd(O_2CCH_3)_2$(Bz_2-bimy)$_2$] (**3**) and *cis*-[$Pd(O_2CCH_3)_2$(Pr,Me-bimy)$_2$] (**4**) in excellent yields of >85%. As noted recently,[2] halo−carboxylato exchange also leads to an improved solubility. Thus, the white complexes **3** and **4** are soluble in most organic solvents with the exception of the less polar ones such as hexane, toluene, and diethyl ether. The improved solubility also results in better resolved ^{1}H and ^{13}C NMR spectra, although the chemical shifts of the carbene ligands remain largely unaffected by the halo−acetato exchange. The $C_{carbene}$ resonances for **3** and **4** amount to 173.3 and 172.5 ppm, respectively, and the presence of the acetato ligands is indicated by signals at 177.1 and 177.8 ppm for the carbonyl carbon atoms. Correspondingly, ^{1}H NMR spectra of **3** and **4** show chemcial shifts at 1.78 and 1.67 ppm for the acetato protons. Furthermore, positive mode ESI mass spectra of **3** and **4** are dominated by $[M - O_2CCH_3]^+$ fragment peaks at m/z = 761 and 513 arising from the loss of one acetato ligand.

Single crystals of complex **3** were obtained from a concentrated acetonitrile solution and subjected to X-ray diffraction analysis. The molecular structure of **3** depicted in Figure 2 confirms the cis arrangement of the carbene ligands around an essentially square-planar Pd(II) center. As commonly observed, they are oriented almost perpendicularly to the PdC_2O_2 coordination plane with a dihedral angle of 82°. The Pd−$C_{carbene}$ bond length amounts to 1.985(6) Å, which is slightly longer than those found in the 1,3-dimethylbenzimidazolin-2-ylidene analogue (1.964(4) Å) probably due to the more bulky N-substituents.[2c] Consequently, the Pd−O bond length of 2.048(5) Å is slightly shorter when compared to that found in the aforementioned analogue (2.076(4) Å). Finally, the pendant oxygen atoms of the two monodentate acetato ligands are found in an anti conformation.

Dipalladium NHC Complexes. In an attempt to study their reactivities, complexes **3** and **4** were treated with 2 equiv of isopropylthiol. An in situ deprotonation of the thiol by the basic carboxylato ligands and subsequent ligand displacement was anticipated, which in turn would lead to the formation of neutral dithiolato-bis(carbene) complexes. However, the targeted neutral complexes were not obtained. Instead, the dipalladium species [Pd_2(μ-iPr-S)$_2$(Bz_2-bimy)$_4$](BF_4)$_2$ (**5**) and [Pd_2(μ-iPr-S)$_2$(Pr,Me-bimy)$_4$](BF_4)$_2$ (**6**) with a [Pd_2S_2] complex core were obtained

upon salt metathesis with $NaBF_4$ as light yellow solids in high yields of 93% and 95%, respectively. The preferred formation of dimetallic complexes bearing two bridging thiolato ligands is apparently due to the highly nucleophilic nature of the latter, which cannot be sufficiently compensated by only one weakly Lewis acidic bis(carbene)Pd(II) complex fragment. It is noteworthy that especially d^8 complexes of the type $[M_2(\mu\text{-}SR)_2L_4]^{2+}$ with various ligands L have received great interest in recent years.[5] However and surprisingly, there exists no example bearing solely NHCs as supporting ligands to the best of our knowledge.

The ^1H NMR spectrum of **5** shows broad signals with a typical heptet at 2.08 ppm and a doublet at 0.68 ppm for the CH and CH_3 protons of the isopropylthiolato ligands. The carbenoid carbon resonances are at 176.0 ppm. The NMR spectra for complex **6**, on the other hand, are more complicated and show the presence of at least three isomers in solution, which result from different arrangements of the unsymmetrical NHC as well as the μ-thiolato ligands. The carbene signal of the main isomer is detected at 174.1 ppm. Positive mode ESI mass spectrometry also supports the formation of complexes **5** and **6** with isotopic envelopes at $m/z = 1642$ and 1147 for the $[M - BF_4]^+$ monocations.

X-ray diffraction on single crystals of both complexes obtained as solvates from concentrated acetone ($\mathbf{5}\cdot 2CH_3CN$) and acetonitrile ($\mathbf{6}\cdot CH_3CN\cdot H_2O$) solutions finally confirmed their identities as dinuclear complexes, and their molecular structures are depicted in Figures 3 and 4, respectively. Both complexes contain two essentially square-planar Pd(II) centers that are coordinated by two terminal benzimidazolin-2-ylidenes and linked by two bridging isopropylthiolato ligands. The carbene ring planes are oriented almost perpendicularly to the PdC_2S_2 coordination planes with dihedral angles ranging from 58.21° to 69.51°, which is commonly observed for NHC complexes. In complex **6**, the two unsymmetrically substituted carbene ligands are also found in the sterically more favorable anti configuration with respect to their N-substituents. When compared to their precursor complex **3** (Pd−C 1.985(6) Å), the $Pd-C_{carbene}$ bond distances in **5** have become slightly elongated, with values of 2.040(11) and 2.045(11) Å, respectively, which is in line with a stronger donation from thiolato as compared to carboxylato ligands. The corresponding distances in **6** are in a similar range. The Pd−S bond lengths of both dipalladium complexes ranging from 2.333 to 2.367 Å are comparable to those found in phosphine analogues.[5f] Noteworthy, the two complexes differ in the bending angle between their two coordination planes. While complex **5** has a planar $[Pd_2S_2]$ ring induced by symmetry and probably due to the steric bulk of the N-benzyl substituents, that of **6** is slightly bent, with a hinge angle of ca. 158°. Consequently, the intramolecular Pd···Pd distance in **5** (3.5026(14) Å) is also longer than that found in **6** (3.4423(6) Å). The intramolecular S···S distances in **5** and **6** amount to 3.1051(41) and 3.1478(24) Å, respectively. As expected, the S-isopropyl groups in **5** are arranged in an anti fashion, pointing to different sides of the planar $[Pd_2S_2]$ ring.

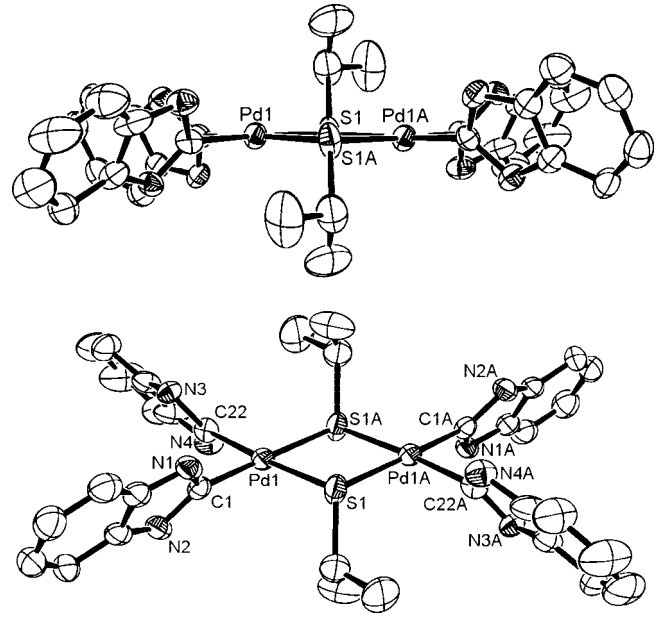

Figure 3. Molecular structure of complex $\mathbf{5}\cdot 2CH_3CN$ showing 50% probability ellipsoids (upper: side view; lower: top view). Hydrogen atoms, solvent molecules, BF_4^- counteranions, and the N-substituents have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 2.040(11), Pd1−C22 2.045(11), Pd1−S1 2.348(3), Pd1−S1A 2.333(3); C1−Pd1−C22 91.4(4), C1−Pd1−S1 91.6(3), C22−Pd1−S1A 93.9(3), S1−Pd1−S1A 83.10(12), Pd1−S1−Pd1A 96.90(12), C1−Pd1−S1A 174.0(3), C22−Pd1−S1 176.4(3).

The same anti arrangement was found in the hinged complex **6**. The latter observation is somewhat surprising, since theoretical calculations would favor a syn orientation of μ-thiolato ligands in complexes with a hinged $[M_2(SR)_2]$ ring.[6]

Conclusion

In conclusion, new dipalladium complexes with a $[Pd_2S_2]$ core solely supported by N-heterocyclic carbenes have been synthesized and structurally characterized. The modular and general methodology presented here widens the scope of NHC ligands in organometallic chemistry beyond catalysis, and research in our laboratory is ongoing to extend this methodology to other transition metals as well as to aromatic thiols.

Experimental Section

General Considerations. If not noted otherwise, all manipulations were carried out without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without further purification if not mentioned. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker ACF 300 and Bruker AMX 500 spectrometers, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^1H, ^{13}C) or externally to CF_3CO_2H (^{19}F). Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Elemental analyses were done on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore. The ligand precursors 1-propyl-3-methylbenzimidazolium iodide and 1,3-dibenzylbenzimidazolium bromide were prepared according to the literature procedure.[3]

***cis*-Dibromobis(1,3-dibenzylbenzimidazolin-2-ylidene)palladium(II) (1).** $Pd(OAc)_2$ (112 mg, 0.5 mmol) was added to a solution of 1,3-dibenzylbenzimidazolium bromide (380 mg, 1.1 mmol) in

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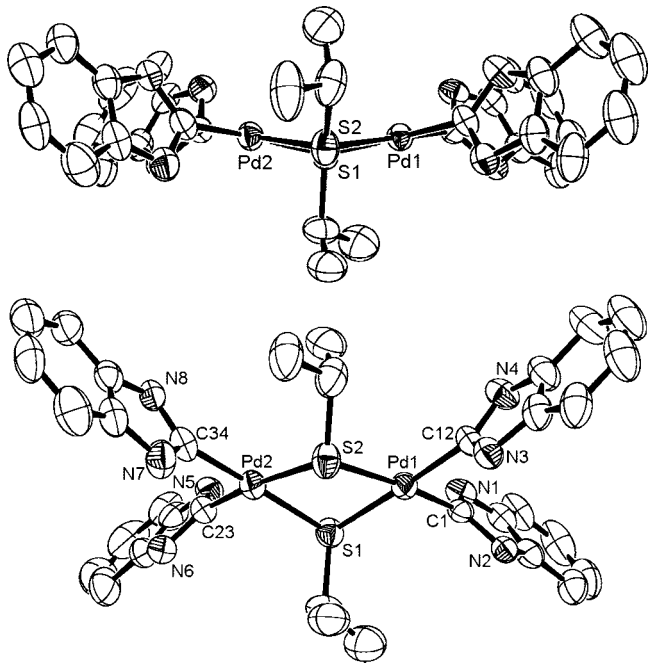

Figure 4. Molecular structure of complex **6**·CH_3CN·H_2O showing 50% probability ellipsoids (upper: side view; lower: top view). Hydrogen atoms, solvent molecules, BF_4^- counteranions, and the N-substituents have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 2.005(6), Pd1−C12 2.035(6), Pd2−C23 2.011(6), Pd2−C34 2.018(7), Pd1−S1 2.3565(16), Pd1−S2 2.3519(18), Pd2−S1 2.3502(17), Pd2−S2 2.3673(16); C1−Pd1−C12 92.4(2), C23−Pd2−C34 94.1(3), C1−Pd1−S1 90.42(16), C12−Pd1−S2 93.24(18), C23−Pd2−S1 88.10(6), C34−Pd2−S2 94.03(19), C1−Pd1−S2 174.27(17), C12−Pd1−S1 177.12(19), C23−Pd2−S2 171.81(19), C34−Pd2−S1 176.4(2), S1−Pd1−S2 83.91(6), S1−Pd2−S2 83.71(6), Pd1−S1−Pd2 94.00(6), Pd1−S2−Pd2 93.67(6).

DMSO (15 mL) and the mixture stirred at 90 °C for 12 h. The resultant yellow suspension was then cooled to ambient temperature and filtered, and the residue was washed with diethyl ether (15 mL). Upon drying under vacuum a white solid (380 mg, 0.44 mmol, 88%) was obtained. ^{1}H NMR (300 MHz, DMSO): 7.20 (br, 20 H, Ph-H), 7.09 (dd, 4 H, Ar-H), 6.86 (dd, 4 H, Ar-H), 6.38 (d, 4 H, ^2J(H,H) = 15.78 Hz, NC*H*H), 5.66 (d, 4 H, ^2J(H,H) = 15.78 Hz, NCH*H*). ^{13}C NMR could not be recorded due to poor solubility of the complex. Anal. Calc for $C_{42}H_{36}Br_2N_4Pd$: C, 58.45; H, 4.20; N, 6.49. Found: C, 58.50; H, 4.26; N, 6.33. MS (ESI): *m*/*z* = 783 [M − Br]$^+$.

***cis*-Diiodobis(1-propyl-3-methylbenzimidazolin-2-ylidene)palladium(II) (2).** $Pd(OAc)_2$ (112 mg, 0.5 mmol) was added to a solution of 1-propyl-3-methylbenzimidazolium iodide (0.332 mg, 1.1 mmol) in DMSO (15 mL). The resultant mixture was stirred at 75 °C for 12 h. The solvent was removed under reduced pressure, and the residue was subsequently washed with water and diethyl ether. Upon drying under vacuum, an off-white solid of cis-anti and cis-syn isomers was obtained in a ratio of 1:0.54 (300 mg, 0.42 mmol, 85%). cis-anti isomer: ^{1}H NMR (500 MHz, DMSO): 7.71–7.65 (m, 4 H, Ar-H), 7.35–7.33 (m, 4 H, Ar-H), 4.40–4.34 (m, 2 H, NC*H*H), 4.30 (s, 6 H, NCH_3), 4.28–4.23 (br, 2 H, NCH*H*), 2.06–1.97 (m, 2 H, CH_2CHHCH_3), 1.81–1.76 (m, 2 H, CH_2CHHCH_3), 0.93 (t, 6 H, $CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (125.77 MHz, DMSO): 173.9 (s, NCN), 134.5, 133.7, 123.3, 111.1, 110.9, (s, Ar-C), 48.6 (s, NCH_3), 37.1 (s, NCH_2), 22.0 (s, $CH_2CH_2CH_3$), 10.9 (s, $CH_2CH_2CH_3$). cis-syn isomer: ^{1}H NMR (500 MHz, DMSO): 7.65–7.61 (m, 4 H, Ar-H), 7.38–7.35 (m, 4 H, Ar-H), 4.70–4.61 (m, 2 H, NC*H*H), 4.51–4.44 (m, 2 H, NCH*H*), 4.18 (s, 6 H, NCH_3), 2.20–2.12 (m, 2 H, CH_2CHHCH_3), 1.96–1.87 (m, 2 H, CH_2CHHCH_3), 1.05 (t, 6 H, $CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (125.77 MHz, DMSO): 174.3 (s, NCN), 134.7, 133.4, 123.1, 111.4, 111.0 (s, Ar-C), 49.8 (s, NCH_3), 35.9 (s, NCH_2), 21.3 (s, $CH_2CH_2CH_3$), 11.0 (s, $CH_2CH_2CH_3$). Anal. Calc for $C_{22}H_{28}N_4PdI_2$: C, 37.28; H, 3.98; N, 7.91. Found: C, 37.47; H, 4.25; N, 8.04. MS (ESI): *m*/*z* = 581 [M − I]$^+$.

***cis*-Diacetatobis(1,3-dibenzylbenzimidazolin-2-ylidene)palladium(II) (3).** AgO_2CCH_3 (75 mg, 0.45 mmol) was added to a suspension of complex **1** (173 mg, 0.2 mmol) in CH_3CN (20 mL). The reaction mixture was stirred for 12 h under reflux conditions shielded from light. The resulting greenish suspension was then cooled to ambient temperature and filtered through Celite to remove precipitated AgBr. The solvent from the filtrate was removed under reduced pressure, yielding an off-white powder (140 mg, 0.17 mmol, 85%). Colorless crystals of **3** were obtained from a concentrated acetonitrile solution upon standing. ^{1}H NMR (300 MHz, $CDCl_3$): 7.12 (t, 3 H, Ar-H), 7.01 (t, 9 H, Ar-H), 6.96 (dd, 4 H, Ar-H), 6.85 (d, 8 H, Ar-H), 6.68 (dd, 4 H, Ar-H), 6.43 (d, 4 H, ^2J(H,H) = 16.44 Hz, NC*H*H), 5.78 (d, 4 H, ^2J(H,H) = 16.44 Hz, NCH*H*), 1.78 (s, 6 H, O_2CCH_3). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): 177.1 (s, O_2CCH_3), 173.3 (s, NCN), 134.2, 133.4, 128.0, 127.1, 125.6, 122.6, 111.4 (s, Ar-C), 52.2 (s, NCH_2), 23.0 (s, O_2CCH_3). Anal. Calc for $C_{46}H_{42}N_4O_4Pd$: C, 67.27; H, 5.15; N, 6.82. Found: C, 67.56; H, 5.34; N 7.17. MS (ESI): *m*/*z* = 761 [M − O_2CCH_3]$^+$.

***cis*-Diacetatobis((1-propyl-3-methylbenzimidazolin-2-ylidene)-palladium(II) (4).** AgO_2CCH_3 (74 mg, 0.44 mmol) was added to a solution of complex **2** (141 mg, 0.2 mmol) in CH_3CN (20 mL). The reaction mixture was stirred for 12 h under reflux conditions shielded from light. The yellow suspension obtained was then cooled to ambient temperature and filtered through Celite to remove precipitated AgI. Removal of the solvent from the filtrate under reduced pressure yielded the product as an off-white powder (103 mg, 0.18 mmol, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.41–7.37 (m, 4 H, Ar-H), 7.30–7.27 (m, 4 H, Ar-H), 4.90 (t, 4 H, NCH_2), 4.47 (s, 6 H, NCH_3), 2.17 (m, 4 H, $CH_2CH_2CH_3$), 1.67 (s, 6 H, O_2CCH_3), 1.17 (t, 6 H, $CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): 177.8 (s, O_2CCH_3), 172.5 (s, NCN), 135.3, 134.1, 124.0, 111.0 (s, Ar-C), 124.0, 110.9 (d, Ar-C), 51.0 (s, NCH_3), 35.4 (s, NCH_2), 24.3 (s, O_2CCH_3), 23.1 (s, $CH_2CH_2CH_3$), 12.0 (s, $CH_2CH_2CH_3$). Anal. Calc for $C_{26}H_{34}N_4O_4Pd$·H_2O: C, 52.84; H, 6.14; N, 9.48. Found: C, 52.79; H, 6.96; N, 9.76. MS (ESI): *m*/*z* = 513 [M − O_2CCH_3]$^+$.

Di-μ-isopropylthiolatotetrakis(1,3-dibenzylbenzimidazolin-2-ylidene)palladium(II) (5). A mixture of complex **3** (82 mg, 0.1 mmol), 2-propanethiol (0.018 mL, 0.2 mmol), and $NaBF_4$ (27 mg, 0.25 mmol) in CH_3CN (12 mL) was stirred at 70 °C for 12 h in a sealed tube. The resulting greenish-yellow suspension was cooled to ambient temperature, and the solvent was removed under reduced pressure. Dichloromethane (10 mL) was added to the residue, and the mixture was filtered through Celite to remove excess $NaBF_4$. The solvent from the filtrate was removed under vacuum to afford the product as a pale yellow powder (127 mg, 0.09 mmol, 93%). Colorless crystals were obtained from a concentrated solution of **5** in acetone. ^{1}H NMR (300 MHz, DMSO): 7.29–6.96 (br, 56 H, Ar-H), 5.89–5.75 (m, 16 H, ^2J(H,H) = 16.26 Hz, NCH_2), 2.08 (m, 2 H, ^3J(H,H) = 6.57 Hz, $SCH(CH_3)_2$), 0.68 (d, 12 H, ^3J(H,H) = 6.57 Hz, $SCH(CH_3)_2$). ^{13}C{^{1}H} NMR (75.4 MHz, DMSO): 176.0 (s, NCN), 134.0, 127.6, 125.7 (br, Ar-C), 133.5, 129.0, 124.2, 112.4 (s, Ar-C), 51.8 (s, NCH_2), 38.1 (s, $SCH(CH_3)_2$), 27.4 (s, $SCH(CH_3)_2$). ^{19}F NMR (282 MHz, DMSO): −72.26 (s, $^{10}BF_4$), −72.31 (s, $^{11}BF_4$). Anal. Calc for $C_{90}H_{86}B_2F_8N_8Pd_2S_2$·$H_2O$: C, 61.83; H, 5.07; N, 6.41. Found: C, 61.26; H, 4.95; N, 6.29. MS (ESI): *m*/*z* = 1642 [M − BF_4]$^+$.

Table 1. Selected X-ray Crystallographic Data for Complexes 2, 3, 5, and 6

	2·0.5Et_2O	**3**	**5**·2CH_3CN	**6**·CH_3CN·H_2O
formula	$C_{24}H_{33}N_4I_2O_{0.5}Pd$	$C_{46}H_{42}N_4O_4Pd$	$C_{94}H_{92}N_{10}B_2F_8S_2Pd_2$	$C_{52}H_{75}N_9B_2F_8OS_2Pd_2$
fw	745.74	821.24	1812.32	1292.75
color, habit	yellow, block	colorless, block	colorless, plate	colorless, block
cryst size [mm]	0.36 × 0.26 × 0.10	0.22 × 0.12 × 0.10	0.40 × 0.30 × 0.14	0.44 × 0.26 × 0.10
temp [K]	223(2)	223(2)	223(2)	223(2)
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	*P*2(1)/*c*	*Pbcn*	*P*2(1)/*n*	*Cc*
a [Å]	10.8524(8)	20.0286(8)	16.6078(6)	27.3460(11)
b [Å]	15.9998(11)	10.1606(4)	15.3151(6)	12.2423(5)
c [Å]	16.1965(12)	18.8389(8)	18.8680(7)	18.1510(7)
α [deg]	90	90	90	90
β [deg]	97.488(2)	90	104.0950(10)	97.0070(10)
γ [deg]	90	90	90	90
V [$Å^3$]	2788.3(3)	3833.8(3)	4654.6(3)	6031.2(4)
Z	4	4	2	4
D_c [g cm^{-3}]	1.776	1.423	1.293	1.424
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	2.899	0.535	0.496	0.734
θ range [deg]	1.80−27.50	2.03−24.00	1.73−24.00	1.50−25.00
no. of unique data	19516	21738	24752	17386
max., min. transmn	0.7603, 0.4217	0.9485, 0.8915	0.9338, 0.8263	0.9302, 0.7384
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0525$, $wR_2 = 0.1211$	$R_1 = 0.0855$, $wR_2 = 0.1580$	$R_1 = 0.1077$, $wR_2 = 0.2501$	$R_1 = 0.0421$, $wR_2 = 0.1022$
R indices (all data)	$R_1 = 0.0750$, $wR_2 = 0.1311$	$R_1 = 0.0914$, $wR_2 = 0.1605$	$R_1 = 0.1178$, $wR_2 = 0.2551$	$R_1 = 0.0452$, $wR_2 = 0.1046$
goodness-of-fit on F^2	1.046	1.332	1.280	1.043
peak/hole [e $Å^{-3}$]	1.620/−0.624	0.860/−1.615	1.029/−0.939	0.784/−0.282

Di-*μ*-isopropylthiolatotetrakis(1-propyl-3-methylbenzimidazolin-2-ylidene)palladium(II) (6). Complex **6** was prepared in analogy to **5** using complex **4** (114 mg, 0.2 mmol), 2-propanethiol (0.037 mL, 0.4 mmol), and $NaBF_4$ (54 mg, 0.5 mmol) in CH_3CN (15 mL) and isolated as a pale yellow powder (200 mg, 0.19 mmol, 95%). Yellow crystals of **6** were obtained from a concentrated acetonitrile solution. ^{1}H NMR (500 MHz, DMSO): 7.74–7.44 (m, 6 H, Ar-H), 7.43–7.38 (m, 10 H, Ar-H), 4.60 (s, 12 H, NCH_3), 4.58–4.56 (m, 2 H, NCH_2), 4.41–4.36 (m, 6 H, NCH_2), 2.17 (m, 2 H, ^3J(H,H) = 6.3 Hz, $SCH(CH_3)_2$), 1.84–1.75 (br, 2 H, $CH_2CH_2CH_3$), 1.66–1.50 (m, 6 H, $CH_2CH_2CH_3$), 1.00 (d, 12 H, ^3J(H,H) = 6.3 Hz, $SCH(CH_3)_2$), 0.71 (t, 12 H, $CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2): 174.1 (s, NCN), 134.8,133.1, 124.7, 124.5, 111.3, 111.2 (s, Ar-C), 50.5 (s, NCH_3), 37.9 ($SCH(CH_3)_2$), 36.3 (s, NCH_2), 27.9 (s, $(SCH(CH_3)_2)$), 22.4 (s, $CH_2CH_2CH_3$), 10.6 (s, $CH_2CH_2CH_3$). ^{19}F NMR (282 MHz, DMSO): −72.28 (s, $^{10}BF_4$), −72.34 (s, $^{11}BF_4$). Anal. Calc for $C_{50}H_{70}B_2F_8N_8Pd_2S_2$: C, 48.68; H, 5.72; N, 9.08. Found: C, 48.32; H, 5.63; N, 8.91. MS (ESI): $m/z = 1147$ $[M - BF_4]^+$.

X-ray Diffraction Studies. Diffraction data for complexes **2**, **3**, **5**, and **6** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 223(2) K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least-squares on F^2 using SHELXL-97[7] with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. A summary of the most important crystallographic data is given in Table 1.

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Supporting Information Available: Crystallographic data for **2**, **3**, **5**, and **6** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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